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GAAS SURFACE PASSIVATION FOR DEVICE APPLICATIONS.(U)
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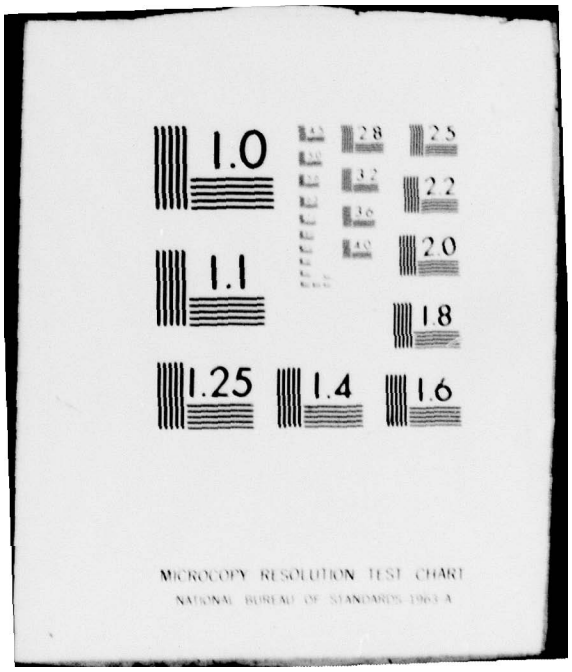
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GaAs SURFACE PASSIVATION FOR DEVICE APPLICATIONS

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This report describes the initial stages of a program to develop deposited dielectrics for GaAs device applications. Three applications of the dielectrics are being investigated: (1) isolation of control electrodes, (2) passivation of the GaAs surface, and (3) encapsulation of completed circuits. The dielectrics being studied include silicon oxynitride; mixtures of silicon nitrode and germanium nitride; and mixtures of silicon dioxide, gallium oxide, and aluminum oxide.

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Deposition techniques being employed are pyrolytic chemical vapor deposition, plasma-enhanced deposition, and photochemical deposition. This report describes the apparatus being used for this program and the chemical analysis of preliminary films deposited. No interface state measurements are reported.

PREFACE

The work reported here is supported by the Air Force Avionice Laboratory, Wright-Patterson Air Force Base, Ohio, under contract F33615-78-C-1444. The Monitoring Engineer is Capt. R.L. Johnson. The program objective is to investigate the passivation of gallium arsenide and the application of dielectric thin film overlayers in metal-insulator-semiconductor field effect transistors.

This work is being performed jointly by the Research Laboratories and the Technology Support Division of Hughes Aircraft Company. Contributions to this work have been made by C.L. Anderson, M.D. Clark, J.W. Peters, R.A. Jullens, and F.L. Gebhart.

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INTRODUCTION AND SUMMARY

The goal of this program is to develop dielectrics that will serve the following three basic purposes in gallium arsenide device technology:

- Passivation – reduction of the number of electrically active centers ("surface states") at the semiconductor surface so that the surface potential can be modulated by control electrodes ("gates") overlying the dielectric.
- Isolation – insulation of control electrodes from each other and from the substrate
- Encapsulation – overcoating of operational circuits to reduce their sensitivity to environmental influences.

To serve these three purposes, Hughes Aircraft Company is developing a variety of deposited dielectrics. Techniques for depositing these dielectric materials are being developed under Hughes internal funding. Evaluation and optimization of these materials for GaAs device applications are being performed under the subject contract.

The following materials are being developed:

- $Ga_xAl_yO_z$ (gallium-aluminum oxide), referred to as (Ga, Al)O
- $Ga_xSi_yO_z$ (gallium-silicon oxide), or (Ga, Si)O
- $Al_xSi_yO_z$ (aluminum-silicon oxide), or (Al, Si)O
- SiO_xN_y (silicon oxynitride)
- (Si, Ge)N (silicon-germanium nitride).

Three basic techniques for depositing these materials are being evaluated:

- Pyrolytic chemical vapor deposition (CVD)
- Plasma-enhanced deposition (PED)
- Photochemical deposition (PCD).

This report describes the progress made during the first six months of the contract. During this period, considerable development and modification of PED and PCD equipment were performed to meet the requirements of this program. Since the pyrolytic reactor, which had been relocated, had not become operational by the end of this reporting period, it was not used for these initial studies. Section 2 describes the equipment being used for this contract and discusses the current capabilities of the various pieces of apparatus.

Using PED and PCD, several dielectric films were prepared and evaluated for chemical composition by auger electron spectroscopy (AES). These studies were helpful in revealing deficiencies in the experimental deposition systems and in obtaining information concerning the dependence of film composition on deposition parameters. The results of these studies are discussed in Section 3. Controlling the composition of PCD films containing nitrogen has been troublesome because of oxygen contamination. More work will be required in this area before these PCD films can be evaluated for device applications. Composition control of PCD oxide films appears to be relatively straightforward.

Before the start of this contract, a proprietary PED film was developed at Hughes. This film has proven highly successful for isolation applications in GaAs integrated circuits (ICs) and planar GaAs charge-coupled devices (CCDs). The composition of this film was disclosed to the Air Force technical personnel monitoring this contract at a program review held at Wright Patterson Air Force Base, 14 November 1978. This material is also being evaluated as an encapsulant for GaAs devices using Hughes internal funding. Because of the success of this material for isolation applications, we have shifted our emphasis toward passivation, the most difficult application of dielectrics in GaAs device applications.

SECTION 2

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The PED system presently being used is shown in Figure 1. The tall unit on the left is an LFE Corporation model PND-301 plasma silicon nitride deposition system modified to permit mass flow control of reactant gases and improved pressure monitoring. The unit on the right is a gas supply cabinet which houses the reactant gases. A schematic of the gas flow system is shown in Figure 2. The units marked "MFC" are mass flow controllers.

In operation, samples are loaded onto the hot plate, which is continuously heated to the deposition temperature. The system is then pumped down to a moderate base pressure of $\sim 10^{-2}$ mm Hg (1 Pa) before the reactant gases are introduced. The flow rates of the gases are then adjusted to the desired values, either by adjusting the MFCs or by monitoring the system pressure using an MKS Baratron capacitance manometer. The flow rates of nitrogen and nitrous oxide are always controlled with the flow controllers. It is more convenient, however, to control the flow rate of silane using the manometer because this avoids the need for frequent recalibration of the silane mass flow controller. On several occasions, decomposition of silane within the unit has caused the silane MFCs to become inaccurate. We have experienced no trouble using the MFCs with dilute germane.

Once the gas flows have stabilized, the rf power is turned on, initiating a glow discharge (plasma) within the chamber. Typical rf powers used in our system are about 65 W. Film thickness is primarily determined by deposition time. The spacing between the silane dispersal ring and the hot plate has a pronounced effect on thickness uniformity but a lesser effect on deposition rate. The effect of the spacing between the hot plate and the rf coils has not been investigated.

Three PCD systems are presently in use. The earliest unit, shown in Figure 3, employs static reactant gases. The chemical reactions employed are induced by mercury photosensitization. That is, 2537 Å uv light excites mercury in the gas phase to a state 5 eV above the ground state:

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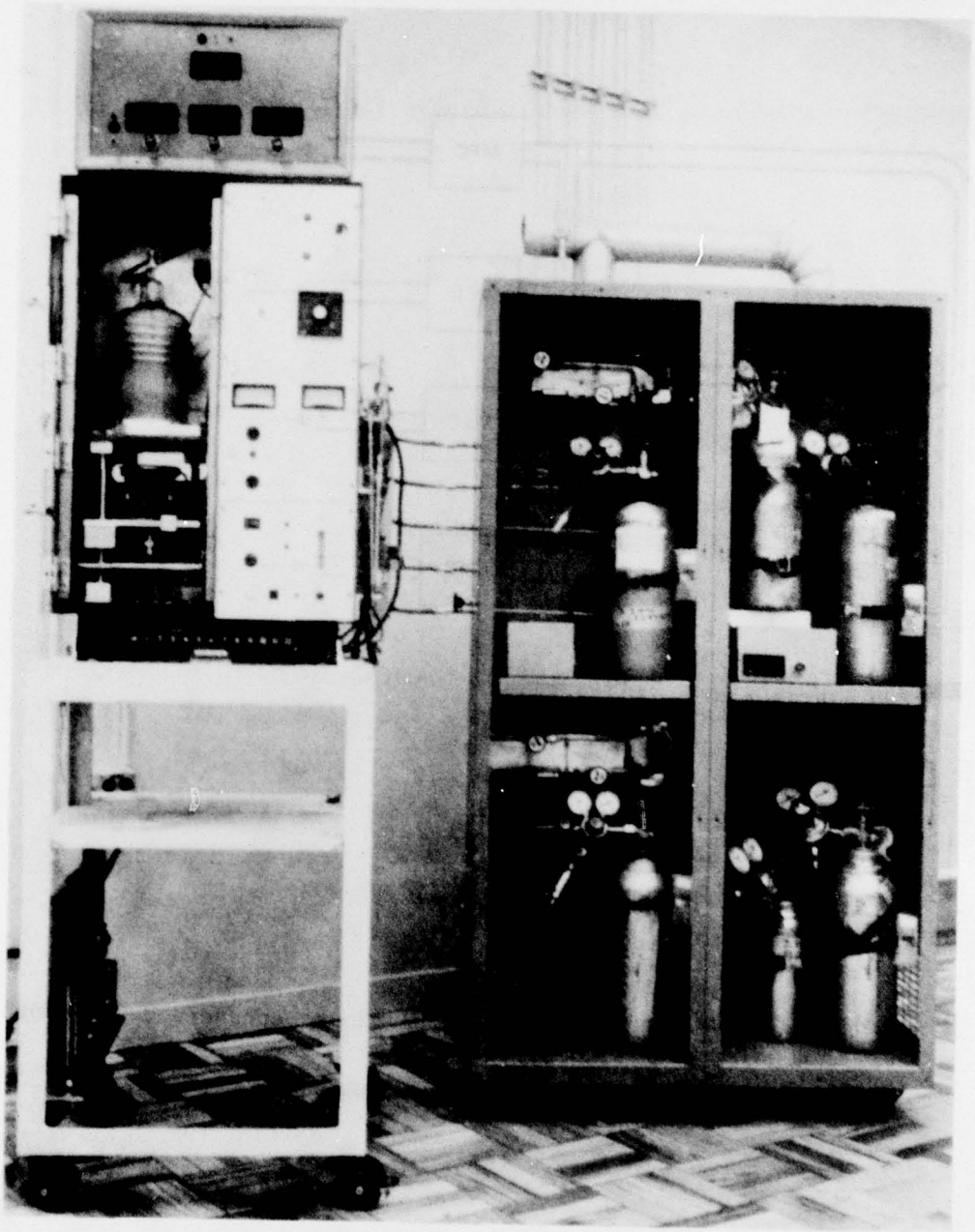

Figure 1. Plasma-enhanced deposition system.

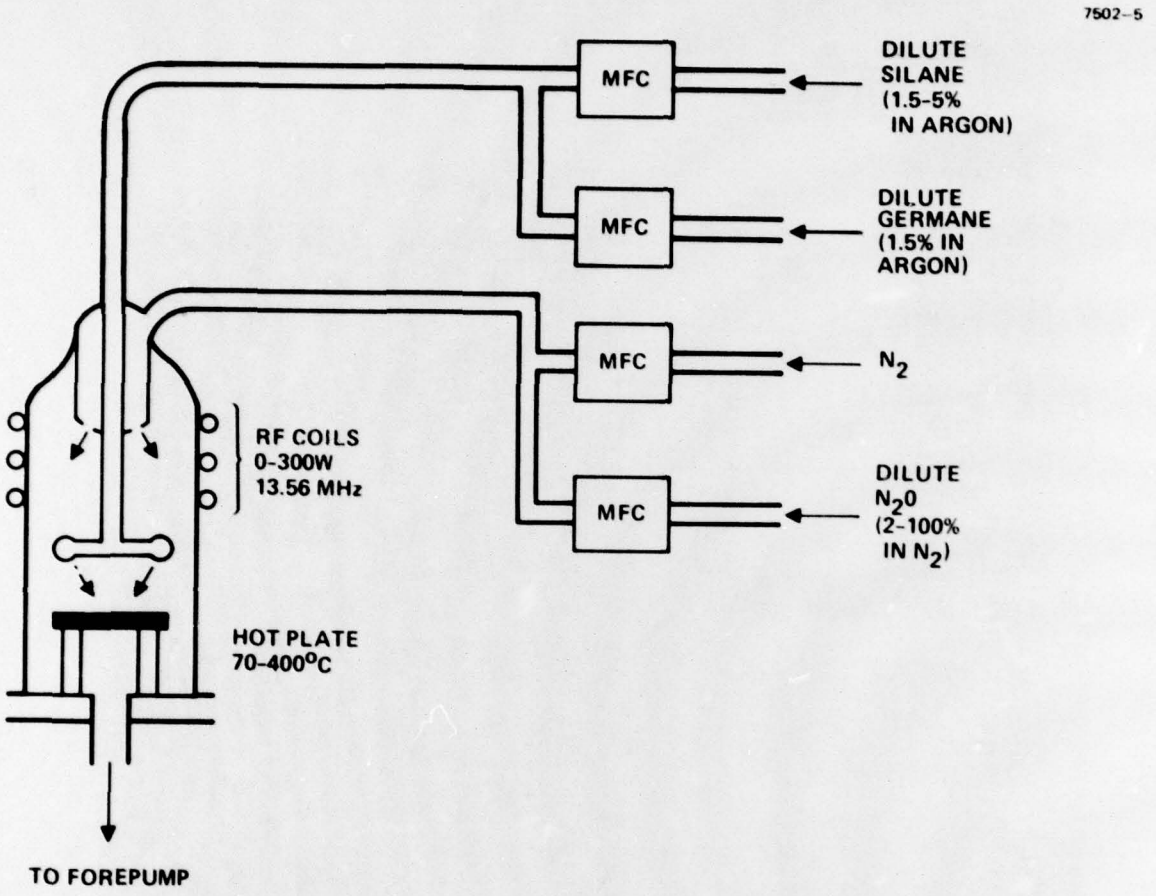

Figure 2. Schematic of gas flow system of the plasma-enhanced deposition system shown in Figure 1.

$$Hg + h\nu\ (2537\ \text{Å}) \rightarrow Hg^{*} \quad , \tag{1}$$

where the asterisk denotes the photoexcited state.

The excited mercury then transfers its excess electronic energy to the reactant gases. For example, silicon nitride can be formed by the process

$$Hg^{*} + 3\ SiH_4 + 4\ NH_3 \rightarrow Si_3N_4 + Hg + 12\ H_2 \quad . \tag{2}$$

Silicon dioxide can be formed by the processes

$$Hg^{*} + N_2O \rightarrow N_2 + O(^3P) + Hg \tag{3}$$

and

$$SiH_4 + 2\ O(^3P) \rightarrow SiO_2 \quad . \tag{4}$$

The static reactor shown in Figure 3 has been used to prepare all the PCD oxides and the PCD nitrides other than silicon nitride studied to date on this contract.

The second reactor, shown in Figure 4, is a production PCD reactor developed in a joint program between Hughes and Tylan Corporation. This "dynamic" reactor unit employs flowing reactant gases and mercury photosensitization. It is capable of depositing a variety of oxides, nitrides, and oxynitrides. It has been used to deposit all the PCD silicon nitride films studied to date on this contract.

The pyrolytic CVD reactor that will be used on this contract is shown in Figure 5. This unit is a helium leak-tight, highly interlocked system capable of growing a wide variety of oxides, nitrides, and oxynitrides with a high degree of composition control. It operates at ambient pressure. Sample heating is produced by rf heating of a graphite susceptor coated with silicon carbide. A feedback circuit permits very rapid variations of temperature to be produced controllably. This capability permits films to be deposited on GaAs at temperatures at which GaAs normally dissociates. For example, silicon nitride can be deposited very rapidly at 700°C. By ramping the sample temperature

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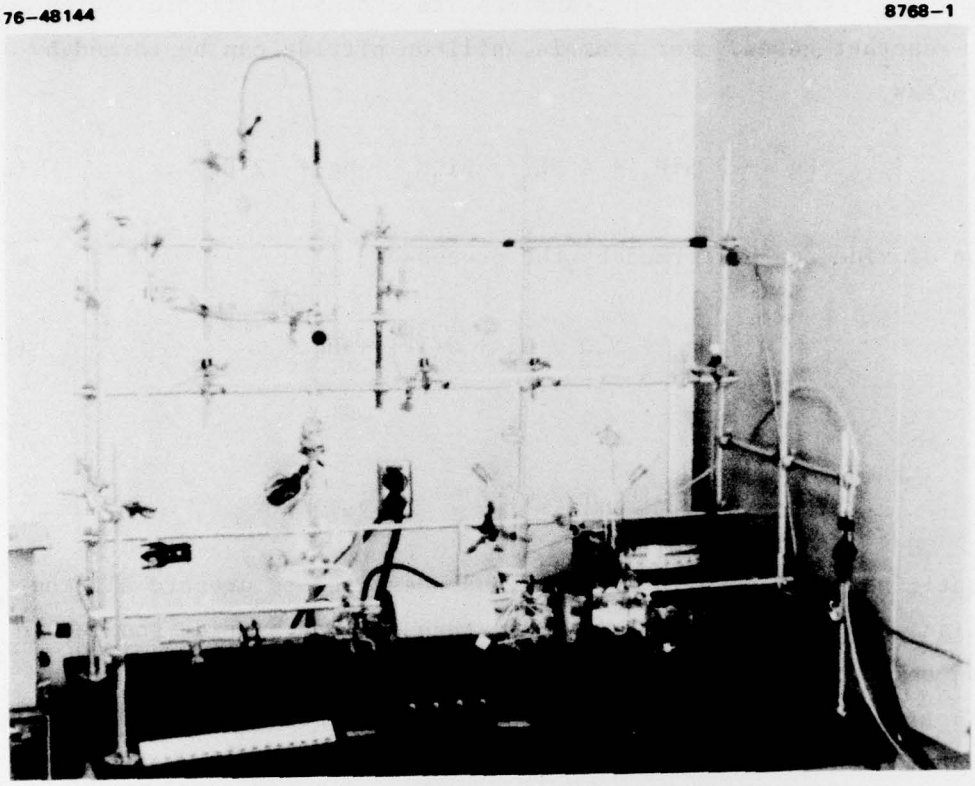

Figure 3. Photochemical reactor using mercury photosensitization and static gases.

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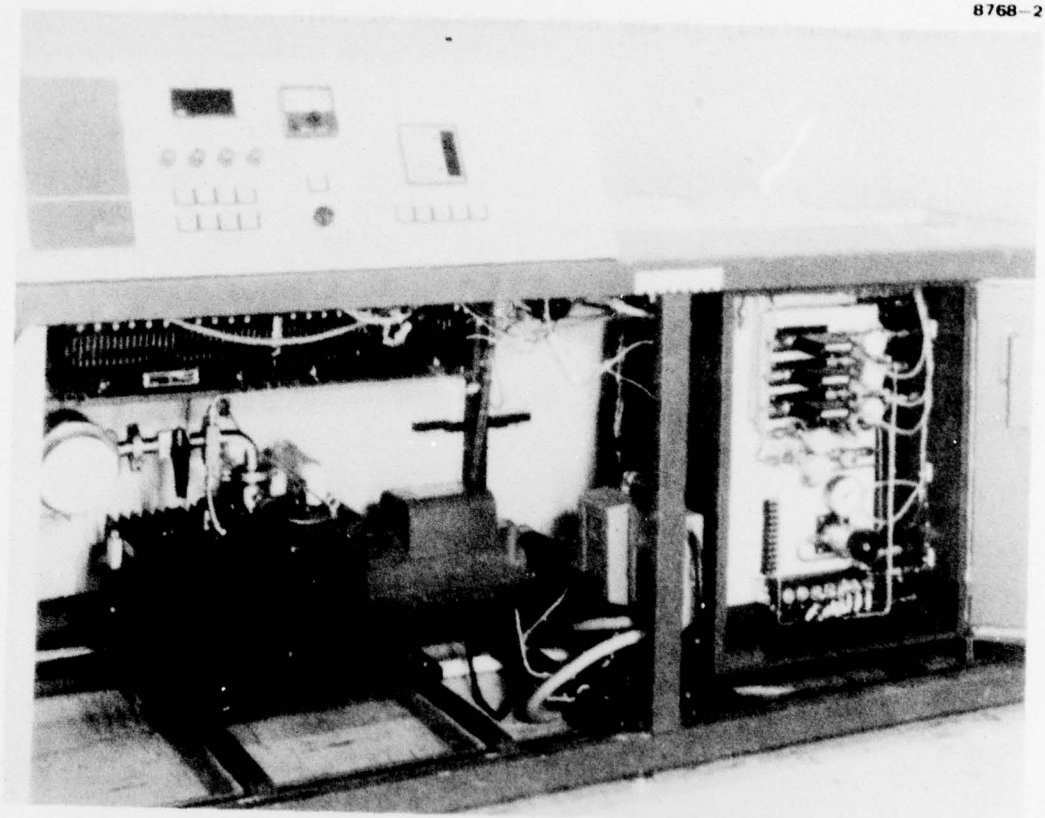

Figure 4. "Dynamic" photochemical deposition system using flowing reactant gases and mercury photosensitization.

from 250°C to 700°C in 9 sec or less, silicon nitride films have been deposited on GaAs with no observable degradation of the GaAs surface. This reactor has been returned to operation following relocation and will be used extensively in the next semester of this program.

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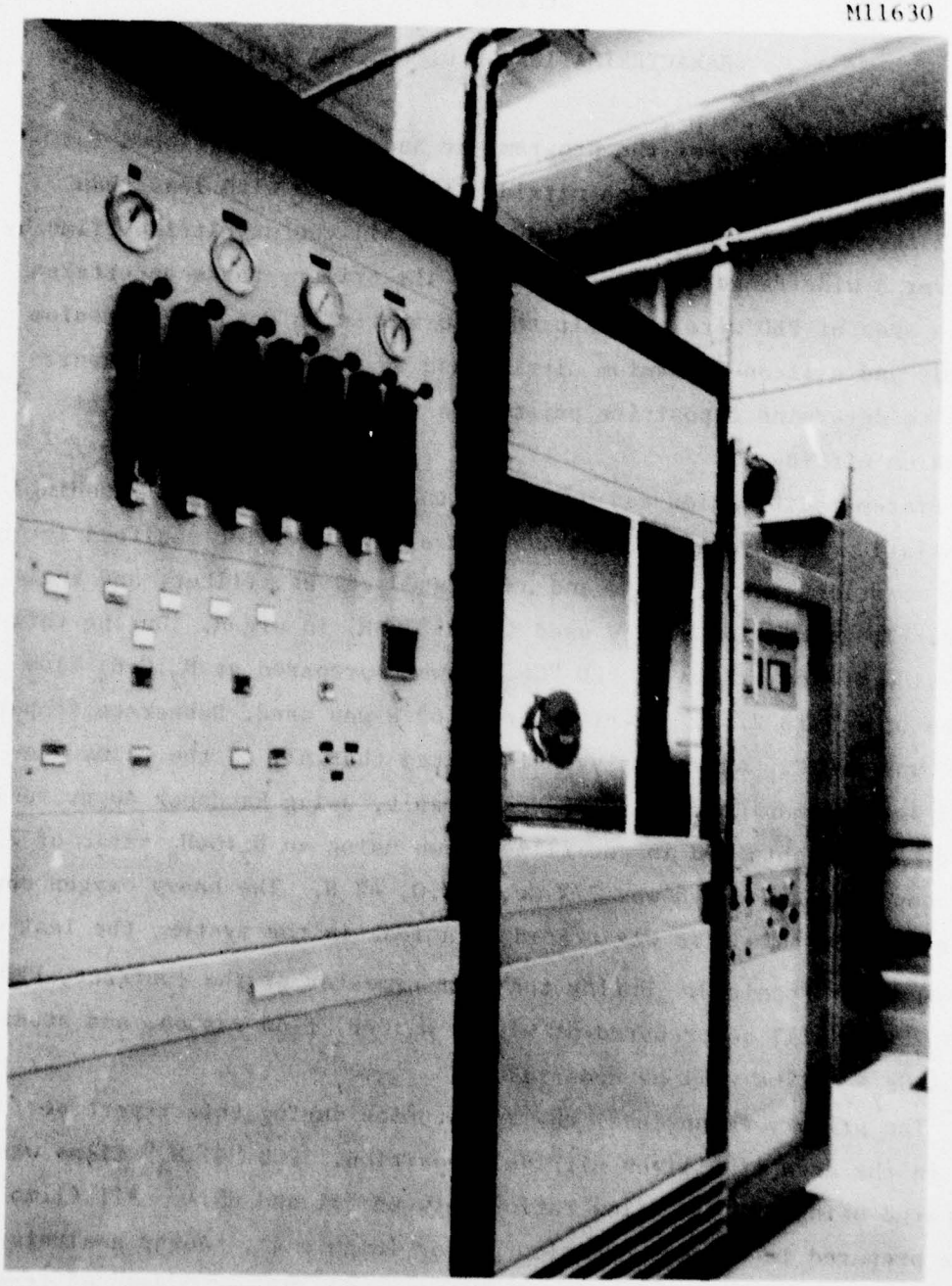

Figure 5. Pyrolytic chemical vapor deposition system.

SECTION 3

CHARACTERIZATION OF DIELECTRIC FILMS

At the beginning of the program, we had already developed the capability to deposit silicon nitride films by PED with less than 5 at.% oxygen contamination and to prepare silicon oxynitride films by PED over a wide range of compositions. The primary tasks undertaken in the area of PED were to equip the PED system to deposit germanium nitride and silicon-germanium nitride and to perform initial experiments to determine deposition parameters that yield stoichiometric germanium nitride.

System modification was performed under Hughes internal funding. The existing PED system was fitted with a germane inlet manifold including a mass flow control unit and associated valves, filter, and regulator. The germanium source used is 1.5% GeH_4 in argon. During this reporting period, films of PED "Ge_3N_4" were prepared at N_2:GeH_4 flow ratios of 7:1 to 27:1. An rf power of 65 W was used. Substrate temperature was 200°C. Auger analysis indicated that all of the films prepared were germanium rich. The best result, using handbook Auger sensitivities, was obtained in the films grown using an N_2:GeH_4 ratio of 27:1. The composition deduced was 77% Ge, 19% O, 4% N. The heavy oxygen contamination of this film was traced to a leak in the system; the leak was subsequently repaired. During the next semester of the contract, PED Ge_3N_4 films will be prepared at higher N_2:GeH_4 flow ratios, and studies of $Si_xGe_yN_z$ films will be undertaken.

The primary emphasis of the PCD studies during this report period was in the area of silicon nitride deposition. PCD "Si_3N_4" films were prepared using NH_3:SiH_4 flow ratios between 5:1 and 65:1. All films were prepared in the gas-dynamic reactor (Figure 4). Auger analysis was performed using sensitivity factors for Si, N, and O deduced from Rutherford backscattering analysis of oxygen-contaminated pyrolytic Si_3N_4 films. The results are presented in Table 1.

TABLE 1. Composition of PCD "Si_3N_4" Films

NH_3:SiH_4 Flow Ratio	5	15	30	65
at.% Si	60	57	46	61
at.% N	22	30	33	33
at.% O	13	7	21	6
at.% C	6	6	0	0
Sensitivies:	Si = 1, N = 0.6, O = 1, C = 0.5			

These results show that increasing the ammonia concentration has a beneficial effect on the Si:N ratio in the films. High ammonia concentrations also appear to result in a lower carbon concentration. (The high level of oxygen contamination in the film grown at a 30:1 ratio of NH_3:SiH_4 is probably the result of a leak in the PCD reactor.) It appears, however, that a further increase in the NH_3:SiH_4 ratio will be necessary to achieve stoichiometric Si:N ratios.

In addition to the PCD "Si_3N_4" films, several other films were prepared by PCD and evaluated by AES. Preliminary "Ge_3N_4" films prepared for this contract were found to be essentially pure Ge and very thin. Films of Ga_2O_3 and SiO_2 prepared in the static reactor were found to be very pure. "Al_2O_3" films were found to contain substantial carbon contamination. This is not surprising because aluminum trimethyl was used as the aluminum source. The fact that the Ga_2O_3 film, prepared using trimethyl gallium, was carbon free, however, indicates that carbon contamination of the "Al_2O_3" films is not necessarily the result of using a metal alkyl.

Hughes internal funding was used to prepare films of "AlN," "TiO_2," and "GaN" by PCD in the static reactor. The TiO_2 film, prepared using titanium chloride as the metal source, was lightly contaminated with carbon; the source of the carbon is unknown. Both of the "nitride" films were heavily oxygen contaminated.

The results to date indicate that it is very difficult to prepare good nitride films in the static PCD reactor. Preparation of oxide films by mercury-sensitized PCD appears to be quite straightforward. Accordingly, we will concentrate on the use of the gas-dynamic system for further PCD nitride studies.

SECTION 4

PROGRAM PLAN FOR 16 DECEMBER 1978 THROUGH 15 JUNE 1979

Because of the success of our isolation dielectric, we will concentrate on gate insulation (passivation) studies for the immediate future. PED films of "Si_3N_4" and (Si, Ge)N will be explored extensively during the next six months. Efforts to reduce oxygen contamination of PCD nitrides will continue. (Al, Si)O and (Ga, Si)O studies will be undertaken next because they require only one organo-metallic source. (Ga, Al)O requires two organo-metallic lines. We do not anticipate that study of the latter system will be undertaken in the next period.

*U.S.Government Printing Office: 1979 — 657-002/101